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14. ABSTRACT

The synthesis of a family of symmetric 2,5-didodecanoxy phenyleneethynylene oligomer series bearing butadiynes as central group was carried out by a Sonogashira-Heck reaction by either the Pd(0)/CuI cross-coupling reaction between a bis(dodecanoxy)benzene halogenate terminated and a bis(dodecanoxy)benzene acetylene terminated oligomer or through self-coupling of bis(dodecanoxy)phenyl acetylene terminated oligomers. The electron-donator character of the dodecanoxy chains favors the acetylene-acetylene coupling in quantitative yields, while the cross-coupling of acetylenes with iodo or bromo-aryls reaction by the Pd/CuI–catalyzed Sonogashira-Heck reaction yields are rather modest. The molecular structure was confirmed by 1H, DEPT-135, APT 13C, COSY, HETCOR and by MALDI-TOF mass spectrometry. The optical properties in solution are quite similar to those of the respective (dodecanoxy) phenyleneethynylenes with high quantum yields with the exception of the dimer due to the fact that it is actually a biphenylbutadiyne. The two photon absorption spectra in chloroform behave according to a three-level model where the conjugation signature S depends on the number of electrons N according to the law: $S=AN^{k}$ with K=4.3.

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ULTRAFAST SPECTROSCOPY OF CHROMOPHORES

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CENTRO DE INVESTIGACION DE QUIMICA APLICADA

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ULTRAFAST SPECTROSCOPY OF CHROMOPHORES

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Grant Objectives: no changes.

Status of Effort: all research objectives have been met.

Summary The synthesis of a family of symmetric 2,5-didodecanoxy phenyleneethynylene oligomer series bearing butadiynes as central group was carried out by a Sonogashira-Heck reaction by either the Pd(0)/CuI cross-coupling reaction between a bis(dodecanoxy)benzene halogenate terminated and a bis(dodecanoxy)benzene acetylene terminated oligomer or through self-coupling of bis(dodecanoxy)phenyle acetylene terminated oligomers. The electron-donator character of the dodecanoxy chains favors the acetylene-acetylene coupling in quantitative yields, while in the cross-coupling of acetyleneswith iodo or bromo-aryls reaction by the Pd/CuI–catalyzed Sonogashira-Heck the reaction yields are rather modest. The molecular structure was confirmed by ^{1}H, DEPT-135, APT ^{13}C, COSY, HETCOR and by MALDI-TOF mass spectrometry. The optical properties in solution are quite similar to those of the respective (dodecanoxy) phenyleneethynylenes with high quantum yields with the exception of the dimer due to the fact that it is in reality a biphenylbutadiyne. The two photon absorption spectra in chloroform behave according to a three-level model where the conjugation signature, S, depends on the number of π electrons, N, according to the law: $S=AN^{k}$ with K=4.3. This value is consistent with strong conjugation resulting from a rod-like shape to the oligomers.

Accomplishments

Molecules that were synthesized per the grant and corresponding spectroscopic properties.

The pathway to synthesize the oligomers (shortly named pPEOC12-Dac) is described in Scheme 1. The convergent synthesis in general involves only two repetitive reactions: a Sonogashira-Heck Pd/Cu cross coupling reaction and desilylation of the protected acetylene groups. In particular, the Pd/Cu cross coupling reactions were carried out by adapting the Godt protocol; where aryliodides are coupled to acetylenes at 0°C, while for the arylbromides the solvent is refluxed at ~ 80 °C in order to effect the coupling reaction.

The oligomerization starts with the Pd/Cu cross coupling of 1 equivalent of **1** and **2** to generate the bromine terminated dimer **3** in 64 % yield. From this reaction, the diacetilene dimer **4** was isolated in a 30 % yield. We observed that in all reactions where the oligomers were acetylene terminated and a Pd/Cu cross-coupling reaction was involved, the diacetylene was always isolated as by-product, but in great amounts. From this fact, we made an exploratory reaction adding the acetylene terminated monomer **1** and the catalyst complex in a typical molar ratio of: $[(C_6H_5)_3P]_2PdCl_2$ (2.5 % mol)/CuI (1.5 % mol) in degassed Et_3N, and we obtained the diacetylene dimer **4** as the main product in 95 % yield. A similar result was obtained in a reaction in absence of CuI, however, longer reaction times were necessary. No differences were observed by increasing or decreasing the palladium catalyst molar ratio as well as when the CuI was incremented to 3.0 % mol; the self-coupling acetylene-acetylene was totally achieved in 2 hours. From these results and for further reactions, we used two CuI molar ratio depending on the coupling type reaction, for instance, in order to favor the coupling between an acetylene and an bromoaryle (~80 °C) or iodoaryle (~0 °C); 1.5 % molar ratio of CuI was determined to be the adequate, while for an acetylene-acetylene coupling reaction; 3.0 % mol provided quantitative yields; keeping always the palladium complex at 2.5 % molar. The bromine terminated dimer **3**, was subjected to a Pd/Cu cross coupling reaction with TMSA affording the dimer **5** in 66 % yields. Desilylation of **5** gave dimer acetylene terminated **6**, which was subjected to a Pd/Cu cross coupling with 1 equivalent of **2** at 0°C to generate the trimer bromine terminated **7** in 59 % yield; the tetramer diacetylene **8** in 37 % yield was also recovered as by product. The acetylene terminated dimer **6** was acetylene-acetylene coupled to form the diacetylene tetramer **8** in 93 % yield. Subsequently, bromine terminated trimer **7** was subjected to another cycle of Pd/CuI coupling with TMS to afford **9** in 63 % that, after its desilylation, gave the acetylene terminated

trimer **10**. Then one equivalent of **6** underwent Pd/CuI cross-coupling to obtain both the bromine terminated tetramer **11** in 46 % yield and the diacetylene hexamer **12** as by-product in 51 % yield. The self coupling of **14** afforded the hexamer **12** in 87 % yield. Finally, the bromine terminated tetramer **11** was subjected to another TMSA cross-coupling-desilylation cycle to form the tetramer acetylene terminated **14**, from which, after its acetylene-acetylene Pd/Cu cross-coupling, the diacetylene octamer **15** was obtained in 89 % yield. The chemical structure was confirmed by NMR and MALDI-TOFF spectroscopy. Figure 1 shows the absorption and fluorescence spectra of the oligomer series in $CHCl_3$ and the linear optical properties are given in Table 1.

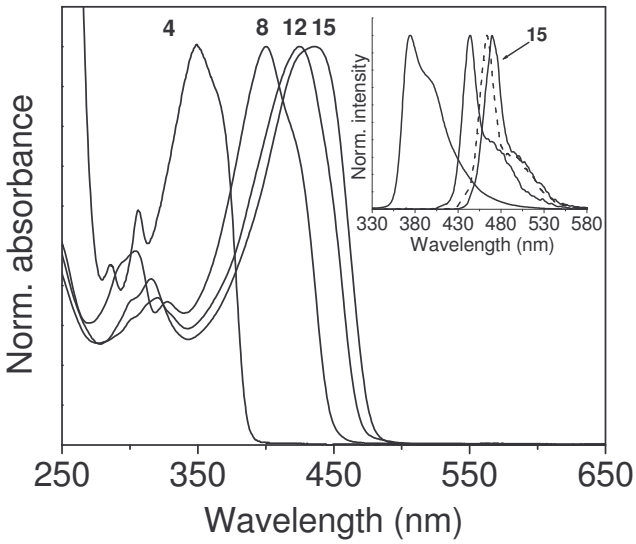

Figure 1. UV-Vis and (inserted) fluorescence spectra of the oligomers in $CHCl_3$. Dimer (**4**), tetramer (**8**), hexamer (**12**) and octamer (**15**).

The following general features can be deduced: 1) the absorption spectra are very broad (BBHW around 70 nm) while the fluorescence spectra are excitonic type with tinier BBHW as the planarization of the geometry in the excited state reduces the conformation distribution with respect to the ground state. The change in the geometry from ground to excited state is confirmed with the Stokes'shift ranging between the value of aromatic systems (around 1430 cm^{-1}) and those of biphenyls, which assume a more planar conformation after excitation (ca. 3310 cm^{-1}). In this respect and in agreement with this literature assessment, the dimer **4** that is a

biphenylbutadyine has the higher value for the Stokes'shift. 2) The absorption spectra present an intense peak due to the HOMO-LUMO transition which red shifts along with the increase of the oligomer length. The corresponding molar absorption coefficient ε increases in the same way according with the larger chromophore content. Higher energy peaks in 300-320 nm range are ascribed to electronic transitions to LUMO from lower lying occupied orbitals. 3) The absorption spectra do not change with concentration or solvent polarity, excluding intramolecular agglomeration (Figure 2a & b). 4) The fluorescence spectra obtained by exciting at different wavelength are identical (Figure 2c) and the excitation spectra when the emission peak is fixed at the more intense peak or to the shoulder are the same confirming that only one emitting state exists (Figure 2d).

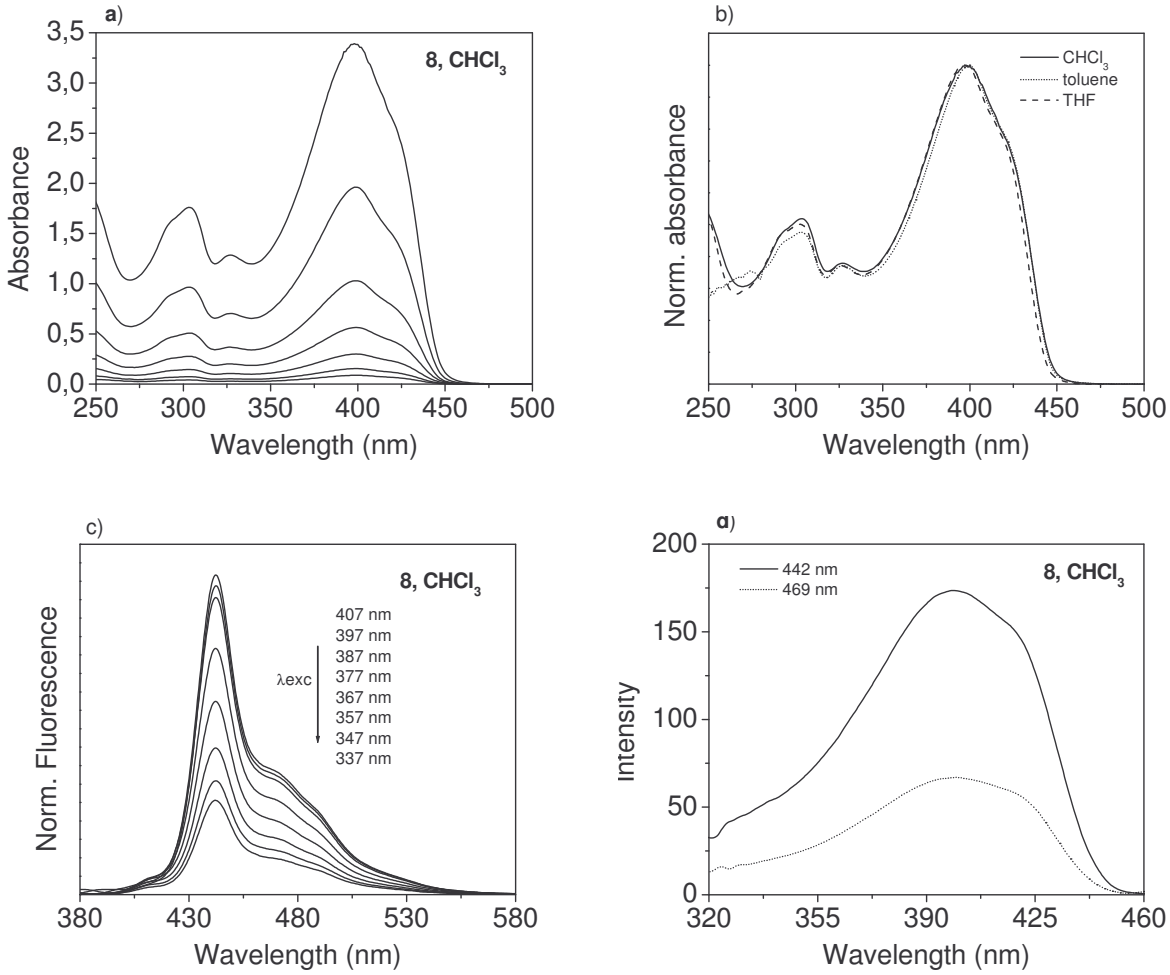

Figure 2. Additional electronic spectra reported for **8** as example. UV-Vis spectra at different concentrations (a) and different solvents (b). Fluorescence spectra at different excitation wavelength (c) and excitation spectra at different emission wavelength (d).

5) Fluorescence quantum yields are very high for the tetramer, hexamer and octamer, in the same range of those reported for H terminated phenyleneethynylene. The dimer presents, on the contrary, a very low quantum yield as for other biphenylbutadiynes and consistently with the larger Stokes'shift.

Table 1. Optical properties of oligomers in $CHCl_3$.

Oligomer	λabs (nm)	HHBWabs * (nm)	ε(M^{-1} cm^{-1}) 10^4	λem (nm)	Stokes' shift (cm^{-1})	E_{S0-S1} (eV)	HHBWfluo* (nm)	Φ_F ** (%)
Dimer (**4**)	350	64	1.68	387	2732	3.37	49	7.4
Tetramer (**8**)	400	68	7.39	444	2477	3.01	23	77
Hexamer (**12**)	425	74	11.60	463	1931	2.74	23	78
Octamer (**15**)	435	77	16.99	470	1712	2.71	24	82

*Half height band width

**estimated error = 10%

These optical properties are thus in general very similar to the dodecanoxy phenyleneethynylenes. However, despite the fact that the dimer indeed absorbs at lower wavelength than the dodecanoxy trimer 3PEOC12-H (350 nm contra 380 nm) and the tetramer between 3PEOC12-H and the dodecanoxy phenyleneethynylene pentamer 5PEOC12-H (412 nm), in accordance with the conjugation. The hexamer and octamer present the absorption maximum at higher wavelength than the heptamer and even the pPEOC12 homopolymer, suggesting that the presence of the central diacetylene group increases the π–π overlapping in the ground state with respect to the phenyleneethynylenes and this overlap is more marked for longer oligomers. Similar behavior was found by Klemm et al. who compared the optical properties of a phenyleneethynylene aldehyde tetramer with those of the corresponding diyne containing oligomer, i.e. the maximum absorption wavelength and relative molar absorption coefficient were higher for the diyne oligomer with respect to the phenyleneethynylene. Based on these results and the chemical structure of the oligomers, no linear optical applications were envisaged and two photon absorption (2PA) spectroscopy was carried out at Montana State University by A. Rebane, et al. in collaboration with Dr. Cooper (AFRL). Two photon absorption (2PA) spectra in

$CHCl_3$ exhibit a weak peak or shoulder corresponding to the S0 → S1 transition. The result indicates that the center of symmetry is broken just enough to give a little bit of permanent dipole moment. A much stronger transition just above the S0 → S1 band is likely a g-g transition that is totally forbidden in the corresponding 1PA. In Figure 3, the 2PA spectrum of the octamer **15** is shown as example together with the 1PA spectrum.

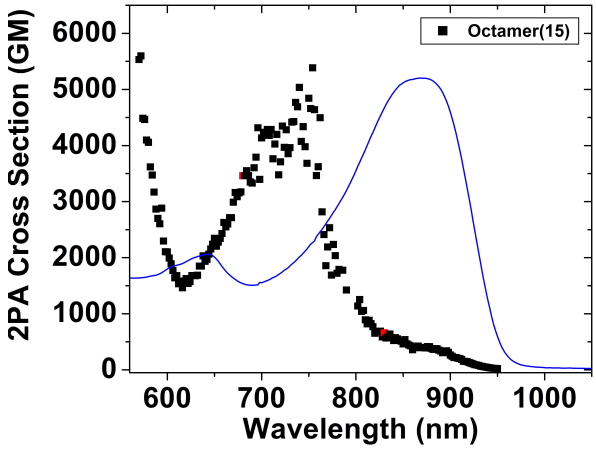

Figure 3. Two photon spectra in $CHCl_3$ for **15**. The abscissa is the excitation wavelength. The ordinate is the 2PA cross section in GM units. Also shown is the 1PA spectrum shifted by 2λ.

The two photon absorption spectroscopy data for the oligomers , **8**, **12** and **15** are reported in Table 2.

Table 2. 2PA spectroscopic data for the oligomers in $CHCl_3$.

Oligomer	N(π)[a]	$\nu_{io}(cm^{-1})$[b]	$\nu_{f0}(cm^{-1})$[c]	$\Gamma(cm^{-1})$[d]	$\sigma_2(GM)$[e]	$S(GM\text{-}cm^{-1})$[f]
Dimer(**4**)	32	28 600	29 850	2 050	8	1.38×10^4
Tetramer(**8**)	64	25 000	29 400	2 050	360	3.62×10^5
Hexamer(**12**)	96	23 500	28 600	2 050	2 100	1.80×10^6
Octamer(**15**)	128	23 000	26 700	2 050	5 000	5.37×10^6

[a]Number of π electrons per oligomer
[b]1PA-allowed transition frequency.
[c]2PA-allowed transition frequency
[d]2PA bandwidth
[e]2PA cross-section
[f]Conjugation signature

The 2PA features shift to the red with increasing chain length more or less the same way as the 1PA spectra. The spectra behave according to a three-level model, so we calculated the conjugation signature *S*, as

$$S = \sigma_2^m \Gamma_f \left(2\frac{\nu_{io}}{\nu_{f0}} - 1\right)^2 = C|\mu_{01}|^2|\mu_{if}|^2$$

where σ_2^m is the 2PA cross section, Γ_f is the 2PA bandwidth(cm^{-1}), ν_{io} is the energy of the 1PA transition(cm^{-1}), ν_{fo} is the energy of the 2PA transition(cm^{-1}). The quantity C is a constant, μ_{01} is the transition dipole moment of the 1PA transition and μ_{if} is the transition dipole moment between the 1PA and 2PA transitions. A fit to a power law gives

$$S = AN_\pi^k$$

Figure 4 is the plot of *S* vs. N_π, where N_π is the number of π electrons in the oligomer. The dependence of *S* on N_π measures the extent of conjugation. When there is strong conjugation through the oligomer, $\mu \sim N_\pi$, giving $S \sim N_\pi^4$. When $k < 4$, the excited states are more localized. For the diacetylene bearing phenylenethynylenes, a value of 4.3 is calculated for k, suggesting strong conjugation resulting from a rod-like shape of the oligomers.

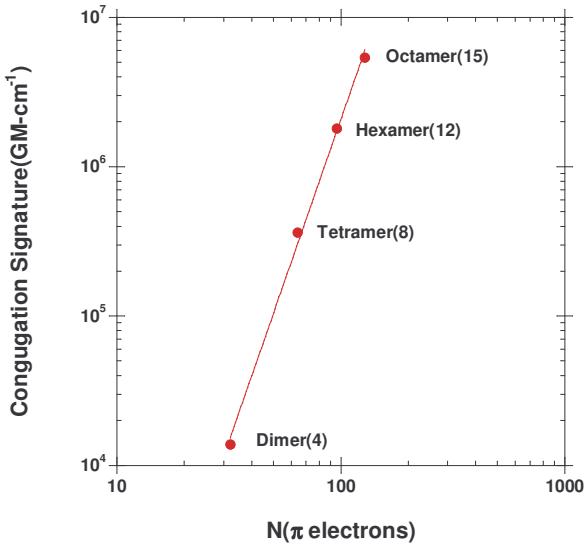

Figure 4. Plot of conjugation signature *S vs*. the number of π electrons in the oligomer series 4Dac **8**, 6Dac **12**, 8Dac **15**. The conjugation signature for 2DAc **4** is estimated from the regression line and is shown for reference.

AFOSR Follow-up. The 2PA spectroscopy data in solution are promising for nonlinear optics application due to large cross sections, especially for the hexamer and octamer. However, ultrafast spectroscopy in solid state films are necessary for the transfer to a device. In this respect,

deep morphological studies in films and structural analysis of the molecules by HRTEM are in progress as these properties affect the effective nonlinear optical performance of the oligomers.

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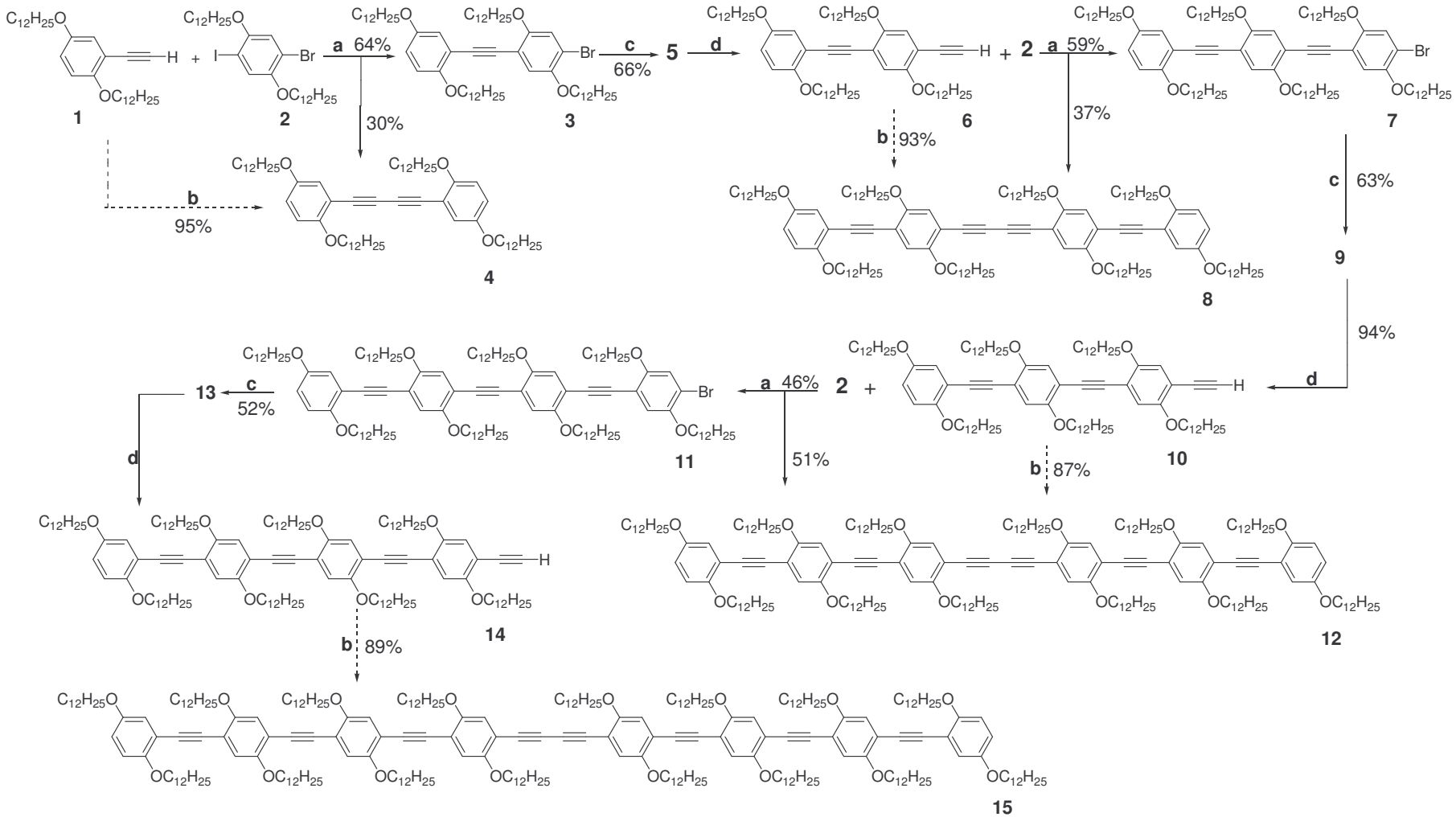
Scheme 1 follows and includes experimental conditions and reagents used.

Personnel Supported: Dr. Eduardo Arias, Dr. Ivana Moggio, Dr. Ronald Ziolo, Ms. Herlinda Gallegos.

New Discoveries: there are no inventions to be patented as a result of this research grant. The results claimed that the new molecules are important for basic research. One scientific publication is in progress.

Scheme 1



Reagents and conditions: (**a**) $[(C_6H_5)_3P]_2PdCl_2$ (2.5 % mol), CuI (1.5 % mol), NEt_3,THF, 0 °C; (**b**) $[(C_6H_5)_3P]_2PdCl_2$ (2.5 % mol), CuI (3.0 % mol), NEt_3, THF, 80 °C; (**c**) $[(C_6H_5)_3P]_2PdCl_2$ (2.5 % mol), CuI (1.5 % mol), TMSA, NEt_3, THF, 60 °C; (**d**) $^{-}F^{+}NBu_4$, THF, rt.